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PLASMA PRODUCTION OF TITANIUM

by

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ABSTRACT

This project deals with a novel application of plasma technology. The results of the production of titanium by plasma decomposition of titanium tetrachloride are presented in this report. The main objective of the work was to demonstrate the technical feasibility of producing dense titanium metal through the thermal decomposition of pure $TiC\ell_4$ plasma.

Pure $TiC\ell_4$ transferred-arc plasma was successfully generated at lower $TiC\ell_4$ flow rates (~1g/min) and a plasma process of producing titanium metal from the plasma dissociation was technically demonstrated on a molten anode surface. The economic feasibility of such a process was not established because of inability to generate a stable plasma at much higher $TiC\ell_4$ flow rates (~50g/min).

It was not possible to establish stable operating conditions for pure $TiC\ell_4$ or a mixture of argon and $TiC\ell_4$ transferred-arc plasma with reasonable flow rates (~10g/min).

It was found that titanium can be produced from a mixture of $TiC\ell_4$ and H_2 introduced into a non-transferred argon plasma. the metal conversion increased significantly from 4.6 to 72 % as the $TiC\ell_4$ feed rate was decreased from 9 to 0.1 g/min. However, the production rate was so low that its commercial feasibility was not established. Finally, it was found that the plasma process can be applied to the production of titanium nitride.

INTRODUCTION

The main objective of this project was to demonstrate the technical feasibility of producing dense titanium metal through the thermal decomposition of pure $TiC\ell_4$ plasma, which is created by a specially designed plasma system. If successful, this plasma process would replace the Kroll process in the current conventional industrial process for the production of titanium sponge from $TiC\ell_4$. It has been shown that the Kroll reduction step is the single most expensive part of the whole plant (1).

The plasma system is of the transferred-arc type, and its design capitalizes on the knowledge and expertise gained by the Plasma Technology Group at McGill during the recent years in this particular area of plasma generation.

Briefly summarized, the plasma system consists of generating vapors of $TiC\ell_4$ in a vaporizer and of feeding these vapors tangentially into an electric arc and of forming a transferred-arc $TiC\ell_4$ plasma, which is thermally decomposed to titanium and chlorine ions and electrons. The ions are neutralized on an anode of molten metal (or titanium) into which the titanium atoms will be accumulated, while the reformed chlorine gas leaves the reactor and collected, to be recycled to the system.

The production of metallic titanium via the plasma route has received a limited amount of attention in the past. All efforts to produce titanium metal by the reduction ot TiO_2 have failed. The only promising route, therefore, has been via its halides. One of the earliest studies is that of Miller and Ayen (2) in 1969, on the reduction of $TiC\ell_4$ vapors in an induction plasma torch operating at low temperatures. Feeding the vapors in an argon plasma resulted in the partial decomposition to the trichloride in good yields, but only when H_2 was added simultaneously to the torch. No titanium metal was produced.

More recently, Akashi and Ohno (3) in 1977 have produced titanium metal, albeit at very low conversion rates, from $TiCl_4$ vapors introduced, together with some hydrogen, into the tailflame of an argon D.C. jet plasma torch. For quite some time, the Electricity Research Centre, in Capenhurst, England, has worked on the reduction of $TiCl_4$ with sodium, both being in the vapor phase, in a hydrogen plasma. Very recently, K.A. Bunting (4) of this Research Centre has presented a report on this approach which indicated that the system was simply too complicated and that the project was being abandoned.

A recent paper summarizes the reduction ot TiO_2 in contact with carbon in a hydrogen plasma flame (5). A pure product was impossible to prepare, as titanium carbide was a persistent impurity.

It is important to note that none of the previous workers in this field has attempted to produce a plasma consisting of the pure halide vapors, which accounts for their failure. It therefore appears that, so far, the originality of the author's concept has been preserved.

Finally, the work of researchers in the plasma arc melting and casting of titanium and titanium alloys, and in particular that of Daido Steel co. in this field, is summarized in a very recent paper by Osawa et al (6).

The purpose of this report is to describe and summarize the progress made during the last two years. The report has been divided into two phases, phase I and phase II. During the first phase, novel equipment were constructed and tested and efforts were concentrated on attempts to obtain the electrical arc properties of a pure $TiCl_4$ plasma. In the second phase, further detailed experiments were carried out to investigate the technical feasibility of producing titanium metal from the novel process developed in phase I.

PHASE I

EXPERIMENTAL

Apparatus

The apparatus used to produce both $TiCl_4$ plasma and titanium metal from $TiCl_4$ plasma is shown schematically in Figure 1. It consisted of the following separate units: D.C. power supply, gas and water supply, control console, cathode assembly, anode assembly, reactor chamber, $TiCl_4$ vaporizer and electric heating units. Each unit will be described individually.

Power Supply

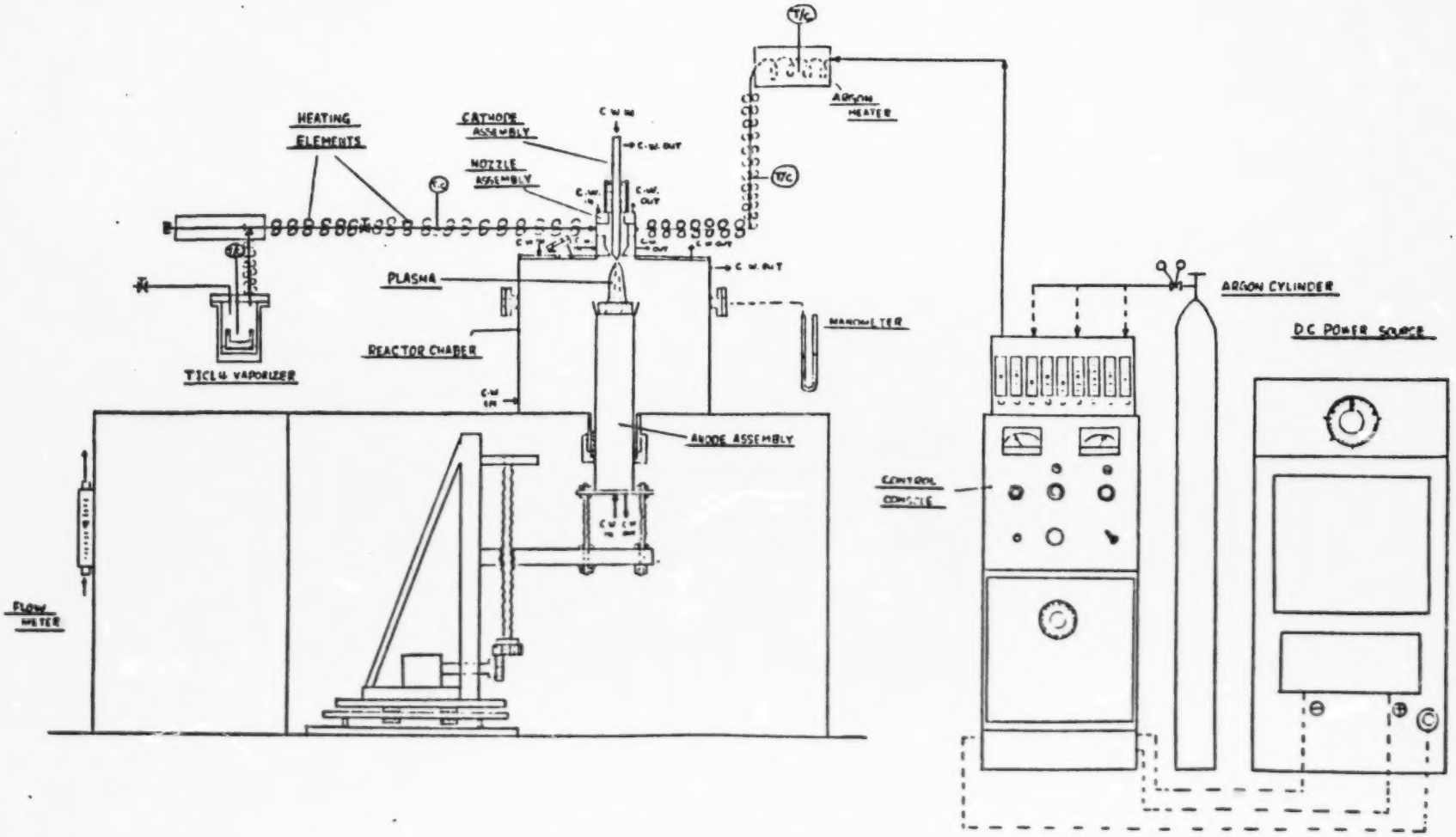
The power was supplied by a 40-kW selenium rectifier, model TDC IA-40, having a drooping characteristic. The input voltage was 3-phase, 60-Hz and 750-volt, while the open output circuits provide 80, 160 or 320 volts. Mainly 160 open circuit voltage was used for the present experiments. The rectifier was connected to a control console, which contained a remote current regulator.

Gas and Water Supply

Industrial grade argon, with a purity of 99.997 %, was suplied from two cylinders, one for plasma forming gas and the other for purging the viewing ports. The outlet gas pressure was regulated by a two-stage pressure regulator. The flows were measured by rotameters attached to the control console. The rotameters were calibrated at 379 kPa. A closed plant water was supplied through a booster pump which discharged the water at 608 kPa.

FIGURE 1

SCHEMATIC DIAGRAM OF EXPERIMENTAL APPARATUS


HEATING ELEMENTS
CATHODE ASSEMBLY
NOZZLE ASSEMBLY
C.W. IN
C.W. OUT
PLASMA
REACTOR CHAMBER
TiCl4 VAPORIZER
ANODE ASSEMBLY
MANOMETER
FLOW METER
ARGON HEATER
ARGON CYLINDER
D.C POWER SOURCE
CONTROL CONSOLE

Control Console

The control console was similar in design to the "Thermal Dynamics" model B60, and was built specially for the present study at Columbia University, New York. It was equipped with all the necessary controls for the high frequency starting system as well as for the gas flow rate and the current flow to the plasma torch. A voltmeter and an ampere-meter were also equipped to record the arc voltage and current.

Cathode Assembly

The cathode assembly, shown in Figure 2, comprised essentially a water-cooled cathode surrounded by a water-cooled concentric nozzle (made of stainless steel 316) and non-water-cooled gas feeding (made of monel). The latter contained two tangential gas injection ports facing each other diagonally. One port was used for $TiCl_4$ vapor coming from the $TiCl_4$ vaporizer and the other for pure argon coming from the main argon cylinder.

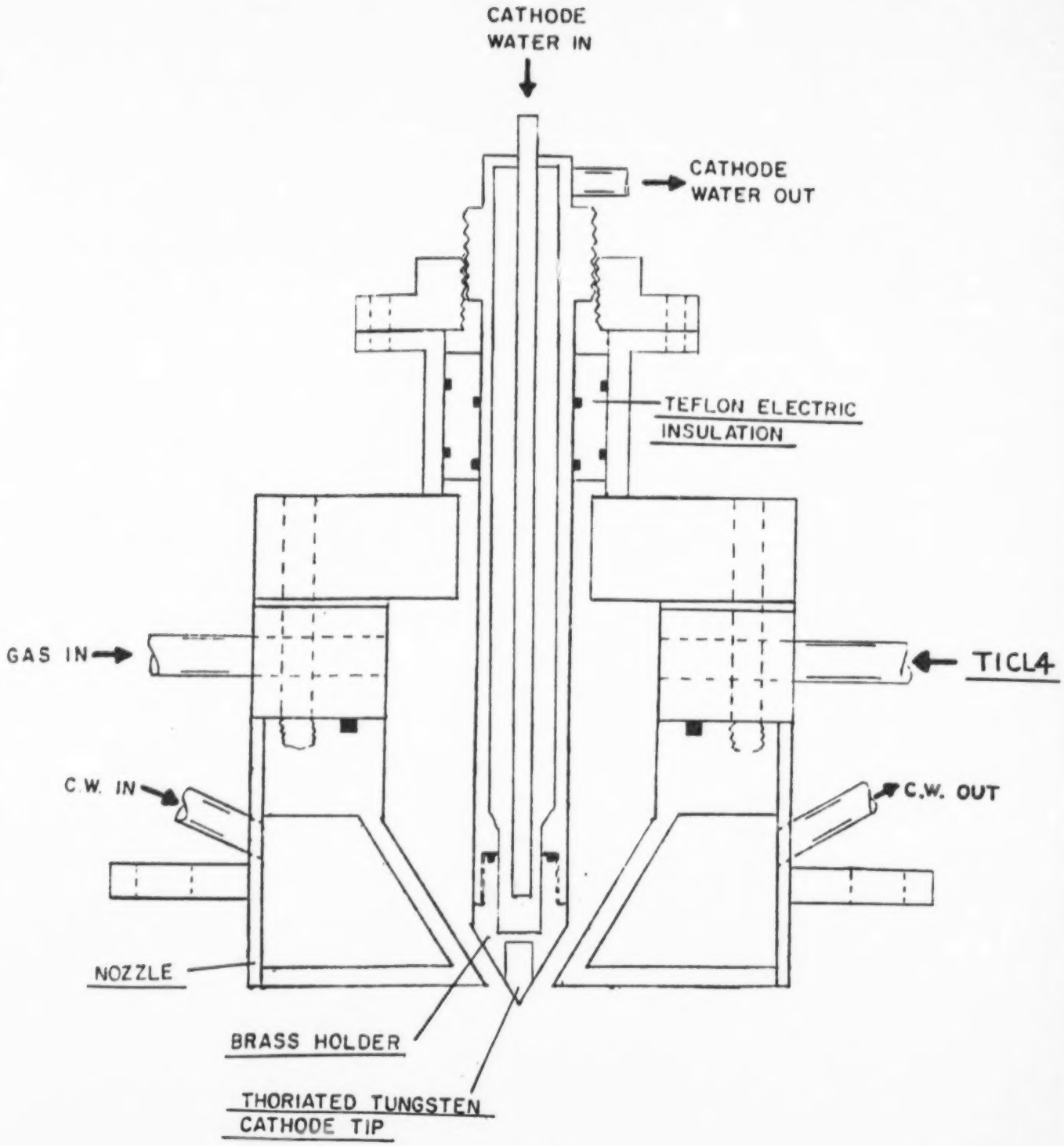
The water-cooled nozzle was designed based on two stringent criteria:

1. No condensation of $TiCl_4$ inside the nozzle;
2. No corrosion of the nozzle.

Initially, a stainless steel (316) nozzle with cooling by hot air or nitrogen was tried but it was experimentally found that the nozzle opening melted due to intense plasma radiation. The suggestion that the nozzle should be made of molybdenum (M.P.: 2890 K) instead of stainless steel was ruled out because of the great difficulty in welding molybdenum and stainless steel. A water-cooled stainless steel nozzle, whose inside was plasma-spray coated with a super fine white alumina powder (METCO 105SF) was tried. The nozzle worked superbly under normal operating conditions without any $TiCl_4$ vapor condensation on its surface. However, the alumina coating

FIGURE 2

CATHODE ASSEMBLY


CATHODE
WATER IN
CATHODE
WATER OUT
TEFLON ELECTRIC
INSULATION
GAS IN
TICL4
C.W. IN
C.W. OUT
NOZZLE
BRASS HOLDER
THORIATED TUNGSTEN
CATHODE TIP

was stripped away after five or six tests. It was thought that the main cause of the stripping was due to the attack of the corrosive $TiCl_4$ vapor in the presence of moisture.

Finally a plain water-cooled stainless steel nozzle without any ceramic coating inside the nozzle was tried. The nozzle worked well without major difficulty except that $TiCl_4$ vapor condensation occurred inside the nozzle. However, the vapor condensation did not prevent the flow ot $TiCl_4$ to the arc, at least for less than 4 g/min. of $TiCl_4$ flow rate. This nozzle has been used for the present tests.

The cathode consisted of a brass tube (1.715 cm O.D., 12 cm long) acting as the cathode tip holder and a conical thoriated tungsten tip. An O-ring was used to seal the joint of the two parts. Inside the brass tube, a stainless tube (0.476 cm O.D.) was silver-brazed at the top and extended to just above the top surface of the tungsten tip. Cooling water entering through the tube impinged onto the tungsten tip and then left the cathode via the annular space between the two tubes. A copper strip was attached to the top of the brass body, serving as a cathode electrical connection. A 2% thoriated tungsten rod (0.25 inch ida.) was silver-brazed to the brass tube and then the tip of the rod was ground to a 60° angle.

In order to avoid $TiCl_4$ vapor condensation and corrosive vapor attack to the outside surface of the cathode tip, the lower part of the surface was coated with high temperature ceramic, called Ceramacoat 512 (manufactured by Aremco Products, Inc.), which is essentially SiO_2.

The vertical position of the tungsten tip was adjustable via teflon sleeves, which were also used to insulate electrically the cathode from the nozzle, the cathode tip protruded slightly out of the nozzle to facilitate easy arc ignition.

Anode Assembly

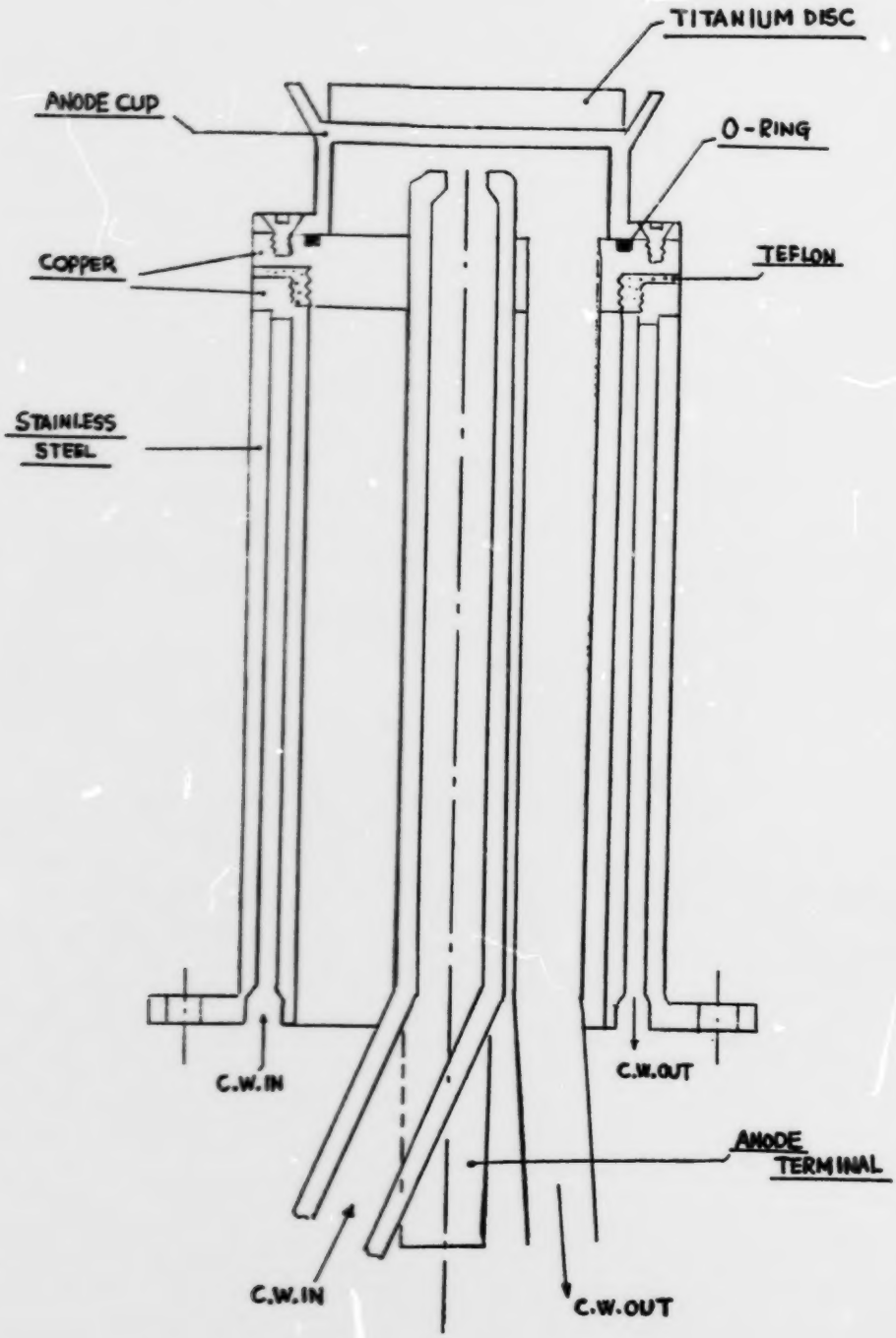
The anode assembly (made of copper) shown in Figure 3 consisted of three parts: the anode cup, the cup holder and the anode assembly holder. The depth and the inside diameter of the cup were determined on the dimension of the initial titanium button. The cup was firmly attached to the cup holder via six flat head machine screws. The central portion of the cup was heavily cooled by cooling water impinging on the back face of the anode, directly beneath the plasma. The cup holder contained an O-ring, coolant inlet and outlet tubes and a thin copper block to which the positive electric cable (or anode terminal) was attached.

The anode assembly holder, made of stainless steel, consisted of a double-walled cylindrical shell (7.62 cm O.D., 30.48 cm long). A small amount of cooling water (less than 0.8 L/min.) was fed to the annular space to prevent overheating of the outside shell. A threaded teflon ring separated the anode assembly holder from the anode cup holder, thus insulating the anode assembly holder electrically.

The anode assembly holder was attached to a vertically movable plate supported by a sturdy metal stand. The plate was remotely controlled by a 0.5 Hp d.c. motor and a fine threaded rod which was attached to the motor shaft. Rotation of the threaded rod permited accurate positioning of the anode assembly in its axial direction. The motor was operated with a precision speed controller and a forward, stop and reverse switch. The whole metal stand also had a pair of rail tracks which provided forward and backward motion. This facilitated the access of the anode assembly to the inside of the reactor chamber.

FIGURE 3

ANODE ASSEMBLY


TITANIUM DISC
ANODE CUP
O-RING
COPPER
TEFLON
STAINLESS STEEL
C.W. IN
C.W. OUT
ANODE TERMINAL
C.W. IN
C.W. OUT

Reactor Chamber

The reactor chamber, as shown in Figure 4, consisted of a top flange, a main cylindrical body and a bottom flange. The top flange (made of stainless steel 316) was water-cooled and had an opening to accomodate the cathode assembly and a viewing port to observe the plasma or measure the temperature of the molten metal bath with an optical pyrometer. The bottom side of the flange was sealed with an O-ring contained between two nylon plastic rings which also served as a thermal and electrical insulator.

The main cylindrical body was water-cooled and contained two viewing ports (5.08 cm dia.) placed at 90° to each other. This allowed for photographic observation of the plasma and for proper adjustment of the cathode tip with respect to the anode surface. The ports consisted of clear quartz glass and provision was made for a stream of argon to pass over them to prevent condensation of $TiCl_4$ vapor during the experiments.

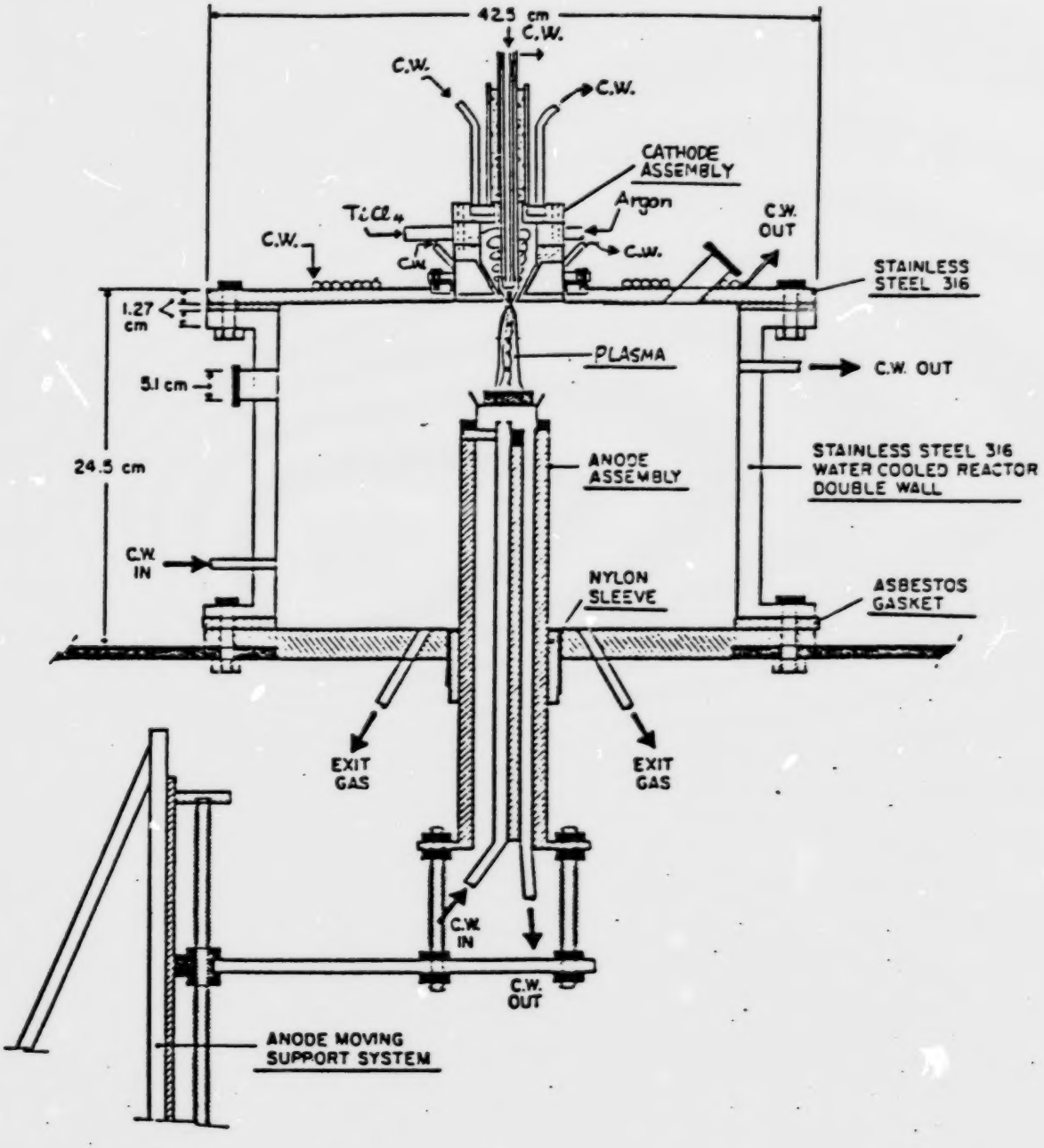
The bottom flange contained an opening for the anode entry and four equally-spaced exhaust gas exits. The latter were designed in such a way as not to disturb the plasma and the plasma tail-flame surrounding the anode. A teflon sleeve containing four O-ring served as a gas-tight seal as well as an electrical and thermal insulator between the anode and the entry opening. Asbestos-based gasket rings were used to serve as a thermal and electrical insulator between the bottom flange and the main cylindrical body.

$TiCl_4$ Vaporizer

The vaporizer was designed and built based on the objecive that the $TiCl_4$ plasma should be sustained a feed rate of 10 g/min. for an experimental duration of 20 minutes. It consisted of a stainless steel 316 cylinder and a top cover of the same material. The top cover contained five openings. Two openings were used for the measurement of the temperature and the pressure of the $TiCl_4$ vapor inside the vaporizer. One opening was

FIGURE 4

PLASMA REACTOR


42.5 cm
C.W.
C.W.
C.W.
CATHODE ASSEMBLY
Argon
$TiCl_4$
C.W.
C.W.
C.W.
C.W.
C.W. OUT
STAINLESS STEEL 316
1.27 cm
PLASMA
C.W. OUT
5.1 cm
24.5 cm
ANODE ASSEMBLY
STAINLESS STEEL 316 WATER COOLED REACTOR DOUBLE WALL
C.W. IN
NYLON SLEEVE
ASBESTOS GASKET
EXIT GAS
EXIT GAS
C.W. IN
C.W. OUT
ANODE MOVING SUPPORT SYSTEM

used for the exit of the vaporized $TiCl_4$ to the main plasma chamber. The two remained openings were used as a by-pass of the excess of $TiCl_4$ vapor and as an auxiliary port which could be used as a carrier gas injection if a carrier gas was needed or a safety pressure relief port in the case of a pressure build-up in the vaporizer.

Electric Heating Units

The argon line and the $TiCl_4$ vapor line leading to the main plasma chamber were heated electrically. Initially medium and heavy duty heating tapes were used to heat the lines and they worked well as long as the heating tapes were not dismantled. However, it was necessary to clean the inside of the lines, especially the $TiCl_4$ line due to the clogging caused by the oxidation of $TiCl_4$. Once the used heating tapes were dismantled from the lines, the tapes became to brittle and fragile and consequently the tapes could not be reused because of the danger of short circuit.

Heating elements were made by inserting nichrome wire (B&S 22, 0.642mm dia., 1.015 ohm/ft) into porcelain beads (sizes 2, 3 and 4). In order to facilitate cleaning of the inside of the lines, the latter were divided into several segments, each of which was wrapped with the required length of heating elements. Four vari arc autotransformers were used to control the entire lines, two for the argon and the others for the $TiCl_4$ lines. The maximum voltage setting of each transformer was limited to the value of six amperes dictated by the known resistance of each heating element. Asbestos tape was wrapped on top of the entire heating elements and Fiberfrax was used in addition for thermal insulation purpose.

EXPERIMENTAL PROCEDURE

1. Preparation of the vaporizer in the glove-box which was under nitrogen atmosphere. This required the following steps:

   a) Transfer $TiCl_4$ liquid into the stainless steel vessel
   b) Place the vaporizer cover (containing the thermocouples) and tighten it with six Allen hexa screws
   c) Weigh the entire vaporizer to the nearest 0.1 g.

2. Connection of the vaporizer exit line to the corresponding $TiCl_4$ feeding line attached to the nozzle.

3. Wrapping of all gas flow lines and of the vaporizer exit line with resistance type heating elements and thermal insulation (or asbestos and Fiberfrax). Preheating of the lines by feeding 50 % of the final power setting of the respective variable transformers.

4. Place a pre-weighed titanium disc into the anode cup.

5. Adjustment of the arc gap for arc initiation by moving the anode assembly.

6. Activating the vacuum pump on to evacuate the reactor chamber for 5 minutes. Repeat the procedure twice.

7. Start to feed cooling water to the needed parts of the equipment and set the variable transformers to the final voltages.

8. Check the temperatures of the cooling water and gas at various locations. Injection of hot argon to the $TiCl_4$ feeding line to eliminate any remaining moisture for three minutes and close the flow.

9. Heat the vaporizer rapidly to the boiling point of $TiCl_4$ (136.4°C) and reduce the heating rate to the vaporizer moderately until $TiCl_4$ vapor temperature reaches about 150°C.

10. Disconnect the main power sources for the variable transformers and all the electronic devices like digital voltmeter, strip-chart record and temperature readout instrument.

11. Turn the rectifier power source on and set argon flow rate to 14 L/min.

12. Make a high-frequency test by readjusting the arc gap. Initiate the argon plasma by pressing the ignition button and set the desired arc length. Immediately resume all the power for the variable transformer and the electronic devices.

13. Start to feed $TiCl_4$ vapor by opening the ball valve at the exit of the vaporizer.

14. Start to reduce the argon flow as soon as the recorded arc voltage starts to rise. Close the argon flow completely when the $TiCl_4$ vapor temperature is at about 138°C.

15. Record all the necessary measurements such as arc voltage, current, cooling water temperature and $TiCl_4$ vapor temperature. Take photos of the $TiCl_4$ plasma (to be precise, a mixture of $TiCl_4$ and argon).

16. Restart feeding argon when the $TiCl_4$ feeding approaches the end and turn the plasma off when the arc voltage returns to the argon plasma voltage at the given condition.

17. Continue to flow argon until the titanium anode is cool.

18. Weigh the titanium anode imediately after it is removed from the reactor.

19. Cool the vaporizer and disconnect the vaporizer from the $TiCl_4$ feeding line. Weigh the vaporizer and record the weigh difference (of the amount of $TiCl_4$ fed).

20. Cool the vaporizer rapidly and precipitate all the remained from the vaporizer by adding dilute NH_4OH and filterate it. Transfer the filtered to an alumina container and burn it at 600°C for two hours. After cooling weigh the amount of titanium dioxide to the nearest 0.1 g.

RESULTS AND DISCUSSION

The results of the experimental work in a pure titanium tetrachloride atmosphere are presented and discussed in this section. Phenomenological observations of the plasma arc and the elecrodes are presented first. The arc voltage dependencies are then shown as a function of a number of parameters to provide information on the electrical characteristics of the arc. However, the results and discussion are very much tentative mainly due to the lack of $TiCl_4$ flow control. Overall energy distribution around the arc are briefly presented. Finally the possibility of producing titanium metal from pure titanium tetrachloride plasma is briefly discussed based on the chemical analysis of the product.

1. Phenomenological Observation

The general appearance of the arc column in a pure titanium tetrachloride plasma is significantly different compared to that in a pure argon plasma. In the former, the color is pinkish yellow and it has two distinct regions, namely, a more luminous central region and a less luminous peripheral region. The arc column of the former is significantly wider than that of the latter under similar operating conditions except the plasma

forming gas flow rate. As the current increases at a given arc length, the diameter and the luminosity of $TiCl_4$ plasma column both increased.

Stable plasma operations, as indicated by the lack of current and voltage fluctuations, were obtained under limited operation conditions. The plasma was stable between 220 and 400 amperes for 3 and 4 cm of arc length at limited $TiCl_4$ flow rates (less than 4 g/min). Due to the limitation of short operating time (less than 10 minutes) and continous variation of $TiCl_4$ vapor flow rate during the run, general criteria for a stable plasma region were not determined. However, it is expected, based on the limited experience of the $TiCl_4$ plasma operation, that an optimum gas flow probably should exist for a given arc length from the arc stability viewpoint.

It was not possible to observe the state of the cathode tip during the run because the cathode tip protruded only slightly from the nozzle opening and the viewing window was clouded by the $TiCl_4$ vapor. Examination of the tip was performed at the end of each experiment. The sharp conical tip was smoothed to a shape, reminiscent of a hemisphere with a small hump (2mm dia.) which may be regarded as a cathode spot. The tungsten tip holder (made of brass) was slightly damaged by both the corrosive hot gas and the thermal plasma radiation near the silver-brazed joint between the tungsten tip and its holder. Although the $TiCl_4$ plasma was never operated at higher current (above 400 A) for more than a few minutes, it was expected that a new cathode tip will be very rapidly deteriorated due to extremely low flow rate of the $TiCl_4$ vapor, which reduces the convective cooling effect on the tip.

The motion of the molten titanium bath acting as an anode could not be observed under the condition of pure $TiCl_4$ plasma unless the viewing port to sight the anode was cleared constantly by purging gas. When a small amount of argon was injected past the viewing port, one could observe the motion of the molten metal and the behavior of the plasma. It was clearly observed that the plasma (or the mixture of $TiCl_4$ and argon) was in a constant motion

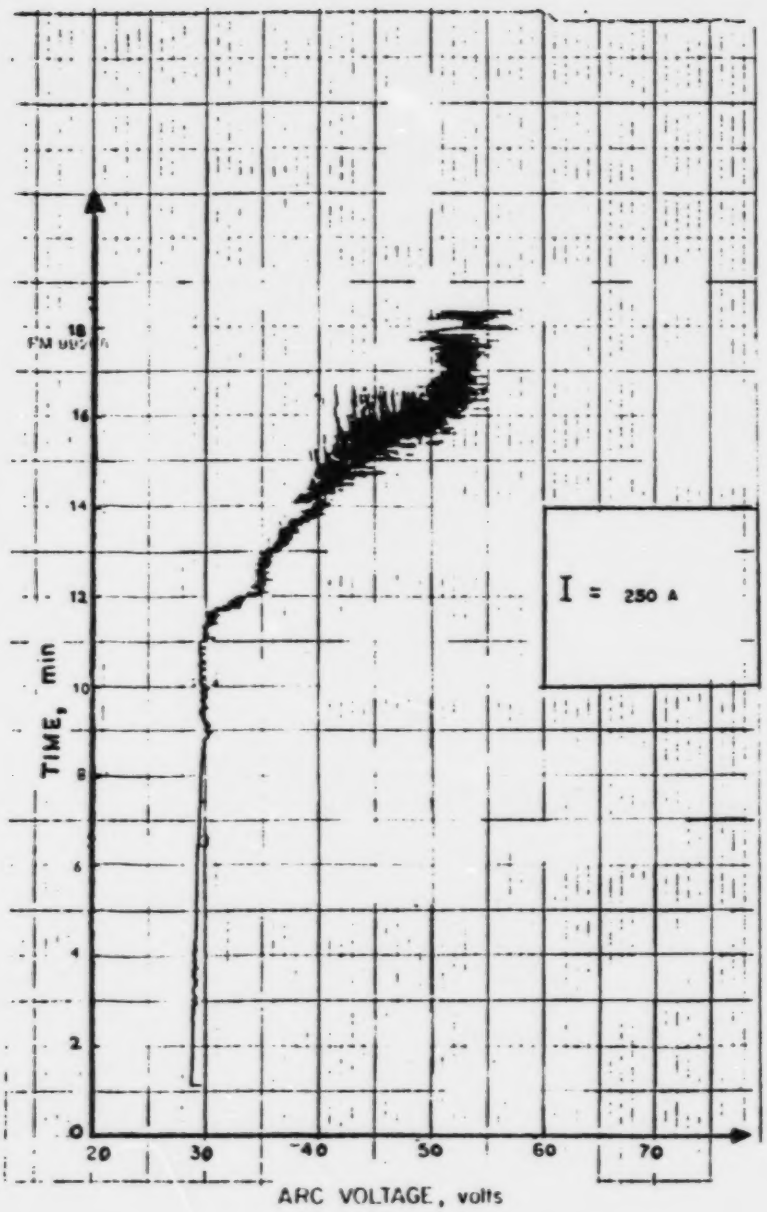
according to the motion of the molten metal. The arc voltage was constantly fluctuated within ± 2 volts once a stable arc condition was established. Abrupt arc voltage variation up to 10 volts did occur at irregular intervals even after a stable arc condition was established.

2. Total Arc Voltage

Due to the uncertainty of stable arc conditions, the initial tests were restricted to fixed arc gap, current and nozzle opening. the only variable parameter was the flow rate of plasma-forming gas (or $TiC\ell_4$), which depended on the heating condition to the vaporizer. A typical arc voltage variation (ℓ=3 cm, I=250 A) with time is shown in Figure 5. The arc voltage was 29 ± 1 volts for pure argon plasma. Small arc voltage fluctuation (less than 0.5 volt) occured at times between 3 and 4 minute, mainly because of titanium metal melting on the anode. As the heating to the vaporizer increased, more $TiC\ell_4$ vapor was generated and resulted in a slight voltage increase (between 4 and 11 minutes). This was expected because the argon flow rate (4.8-7.5 L/min) was far higher than the $TiC\ell_4$ flow rate (~0.2 L/min.). The arc voltage started to rise rather rapidly after the vapor temperature reached 138.9°C ($TiC\ell_4$ B.P.=136.4°C). It was at this time that significant amount of $TiC\ell_4$ vapor was considered to be generated. Argon flow was gradually cut off and completely shut off a few minutes later when the arc voltage still rose. It took a couple of minutes before all the remained argon in the reactor chamber was consumed. When pure $TiC\ell_4$ was generated, the arc voltage was expected to be steady. Betwen 16 and 18 minutes of operation, the arc voltage was 52±2 volts. It was considered that the arc was stable and the $TiC\ell_4$ feed rate was almost constant during those periods. The arc voltage started to increase again beyond 18 minutes of the test and shortly later the arc abruptly extinguished. It was very difficult to pinpoint the cause of arc termination. One of the possible explanations, however, could be as follows: since the heating rate to the vaporizer is maintained constant for a given initial $TiC\ell_4$ charge, the rate

FIGURE 5

ARC VOLTAGE VARIATION WITH TIME

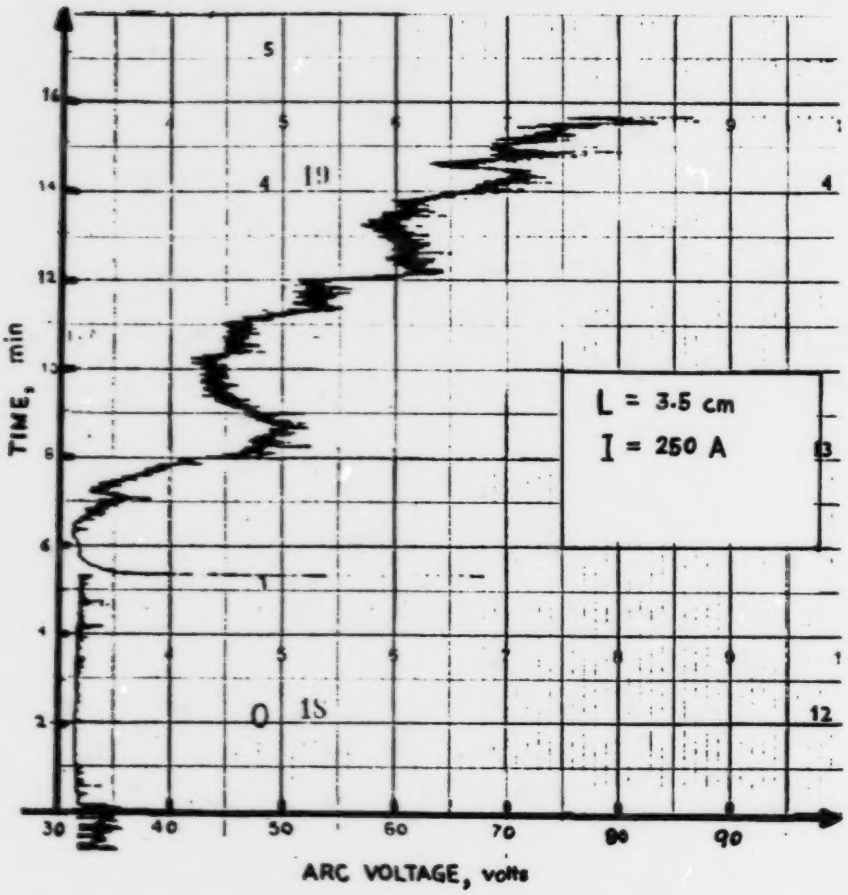

TIME, min
0
2
4
6
8
10
12
14
16
18
20
30
40
50
60
70
ARC VOLTAGE, volts
I = 250 A

of $TiCl_4$ vaporization increases as the experiment progresses. However, the average $TiCl_4$ feed rate at the conditions is estimated to be about 0.5 L/min which is far less than the argon flow rate (7-14 L/min.). In addition, the ionization potential of $TiCl_4$ is much higher than that of argon. Thus, those two combined factors (or $TiCl_4$ flow rate and higher ionization potential) creates the state of ion deficiency in the plasma at given arc currents (250-300 A). When this happens, the plasma arc voltage will go up because of very low electrical conductivity of the plasma and the arc current will drop accordingly at a given power input. Since the arc voltage fluctuation occurs in a very short period time, if the arc current is not adjusted in time according to the voltage fluctuation, the arc current falls below the value at which the arc can be sustained. When one increases the total arc power input in order to sustain the arc, significant titanium metal loss from the molten titanium bath was experienced due to vaporization.

When the heat input to the vaporizer increases rapidly, the arc voltage variation with time is shown in Figure 6. Obviously, the $TiCl_4$ feed rate changed constantly. $TiCl_4$ feeding started even before its boiling point, due to its rising vapor pressure in the vaporizer. When the temperature of $TiCl_4$ was around 100°C, the arc voltage reached above 50 volts even with 5 L/min of argon flow. After 14 minutes of arc operation, argon flow was increased intentionally to 7.5 L/min hoping to reduce the voltage fluctuation. Momentarily, the arc voltage dropped back to 65 volts and climbed to higher voltage. When the $TiCl_4$ vapor temperature was at its boiling point, the arc voltage was around 75 volts with 5 L/min of argon flow and shortly after the arc exginguished. As far as the operator is concerned, there is very little time to manipulate the arc controls in order not to extinguish the plasma, when the arc current goes below the point where the plasma can be sustained. Two things may be exercised to sustain the plasma; one is to increase the arc power input by increasing the arc current at given arc length and gas flow rate, and the other is to raise the arc length and gas flow rate, and the other is to raise the arc length which causes the arc

Figure 6

Arc Voltage Variation with Time


TIME, min
ARC VOLTAGE, volts
L = 3.5 cm
I = 250 A
30
40
50
60
70
80
90

voltage to increase and consequently increase the total arc power input at a given arc current and gas flow rate. Unfortunately, the former is limited to the arc current above which significant metal loss from the molten anode bath may occur. In the latter, the plasma is likely to be less stable and the power efficiency to the anode will be reduced.

It appears that the arc voltage of pure $TiC\ell_4$ plasma will increase even more than 90 volts as $TiC\ell_4$ feed rate increases. It is uncertain at this moment whether there is a maximum $TiC\ell_4$ feed rate at given conditions above which the plasma is no longer stable. Thus, the general electrical characteristics (relationship among arc voltage, current, length and vapor flow rate) for pure $TiC\ell_4$ plasma cannot be obtained until a dependable $TiC\ell_4$ feeding system is available. A new vaporizer, made of glassware and electrical heating unit for the vaporizer are being prepared.

3. Overall Energy Distribution

As mentioned before, the experimental conditions were limited due to the inability to control the $TiC\ell_4$ feed rate to the arc and the results are not sufficient to establish the relationship among the operating conditions. Briefly speaking, 38-55 % of the total arc power was transferred to the molten anode and less than 5 % of that went to the cathode tip. About 25 % of the total arc power was transferred to the nozzle in the form of radiation and the remained was dissipated as a direct radiation from the plasma.

4. Recovery ot Titanium Metal

Because of small leaks from the main reactor chamber, the produced ingot contained impurities like oxygen and hydrogen. Chemical analysis of a sample showed 0.88 % of exygen in the product, while the initial charge (commercially available titanium metal) had 0.14 % of oxygen. Based on the

assumption that the same amount of oxygen is contaminated in the product, the conversion was estimated to range between 8 and 52 %. The $TiCl_4$ feed rates were 0.7-3.6 g/min. However, the specific power consumption of the produced titanium was excessively high mainly because of very low $TiCl_4$ feed rates. When small amount of hydrogen was added to the $TiCl_4$ vapor, the conversion was improved significantly. No direct quantitative comparison between with H_2 and without H_2 were attempted since different $TiCl_4$ feed rate were used.

Further detailed tests are required to establish the relationship among those operating variables after the main reactor chamber is completely sealed. The optimization of the process will be pursued in the second phase of the present project (1984).

CONCLUSIONS

The following conclusions can be made based on the limited results:

1. Pure $TiCl_4$ plasma was succesfully created by a specially designed plasma system and the production of titanium metal was positively identified.

2. Pure $TiCl_4$ plasma arc voltage (I=300A, L=3cm and $TiCl_4$ feed rate = 1.7-3.6 g/min.) was determined to be 52+2 volts.

3. The metal conversion was estimated to range between 8 and 52 % based on assumed oxygen content in the product.

4. A reliable $TiCl_4$ feeding system and an air tight plasma reactor are required to obtain more detailed and reproducible data.

PHASE II

EXPERIMENTAL

The apparatus and procedure used in the work of phase II are generally similar to those used in phase I. Only modifications or improvements will be described in the present section.

Apparatus

The apparatus used in phase II is shown schematically in figure 7. It consisted of the following separate units: power supply and control console, gas and water supply, cathode assembly, anode assembly, reactor chamber, $TiCl_4$ vaporizer and electric heating units.

Power Supply and Control Console

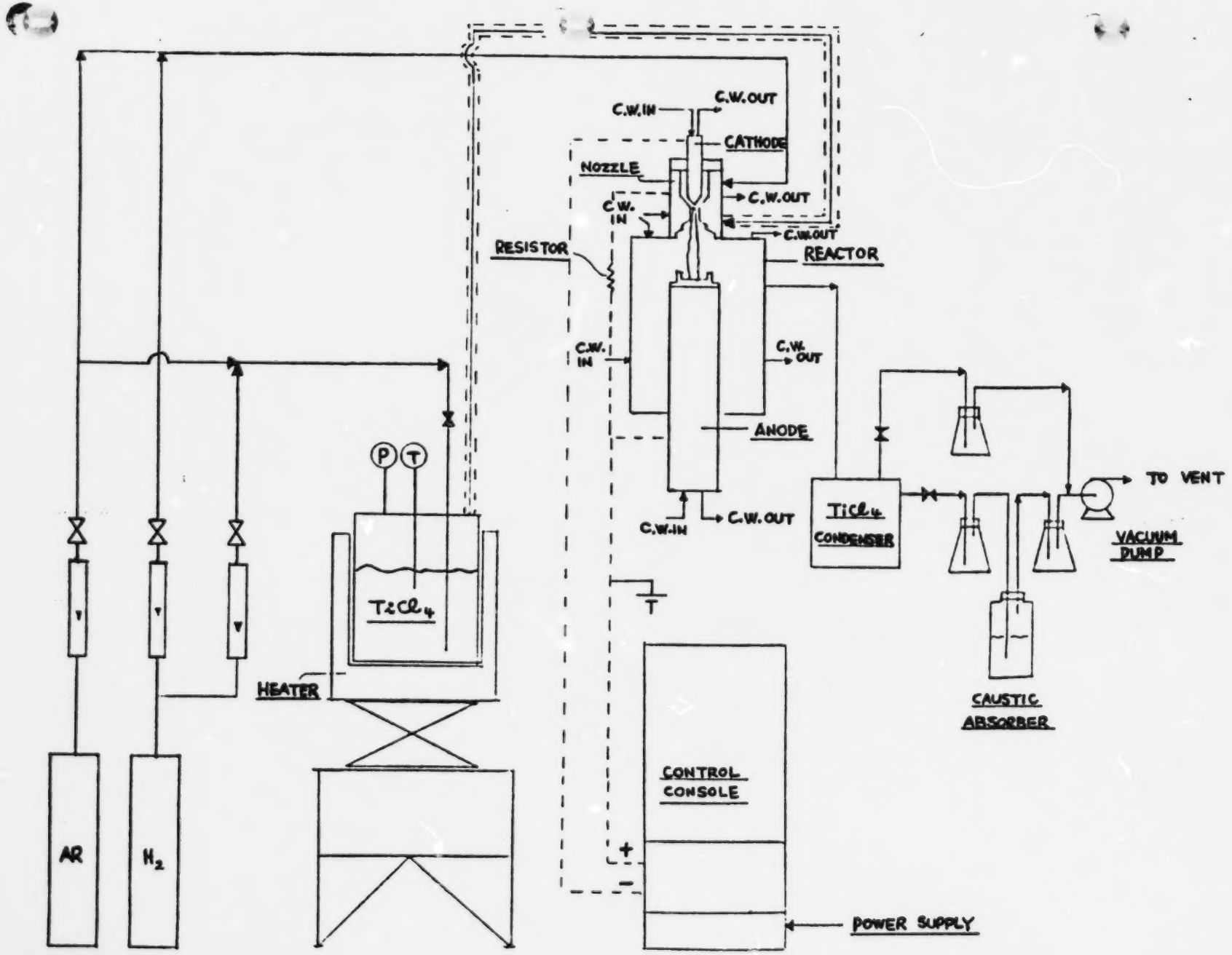
The power was supplied by a 75-kW silicon rectifier, model SR-1500 F7, having a drooping characteristic and 100% duty cycle rating. The input voltage was 3-phase, 60-Hz and 600-volt, while the triple open output circuits provide 100, 200 or 400 volts. Mainly 200 open circuit voltage was used for the present experiments. The rectifier was connected to a removable and remote control console, which was equipped with voltmeter, ammeter, remote contactor, current and start control. A separate high frequency arc stabilizer superimposed high frequency energy on d.c. power supply secondary outputs.

Cathode Assembly

Two different cathode assemblies are used in this work. The earlier one, shown in Figure 2, was constructed based on a 'FCC' (Fluid Convective Cathode) design and is the same one used in the work of phase I. The second one, shown in Figure 8, was constructed based on a "wall-stabilization"

FIGURE 7

SCHEMATIC DIAGRAM OF EXPERIMENTAL APPARATUS


C.W. IN
C.W. OUT
CATHODE
NOZZLE
C.W. OUT
C.W. IN
C.W. OUT
RESISTOR
REACTOR
C.W. IN
C.W. OUT
ANODE
C.W. IN
C.W. OUT
TiCl4 CONDENSER
TO VENT
VACUUM PUMP
CAUSTIC ABSORBER
P
T
T2Cl4
HEATER
T
CONTROL CONSOLE
+
-
POWER SUPPLY
AR
H2

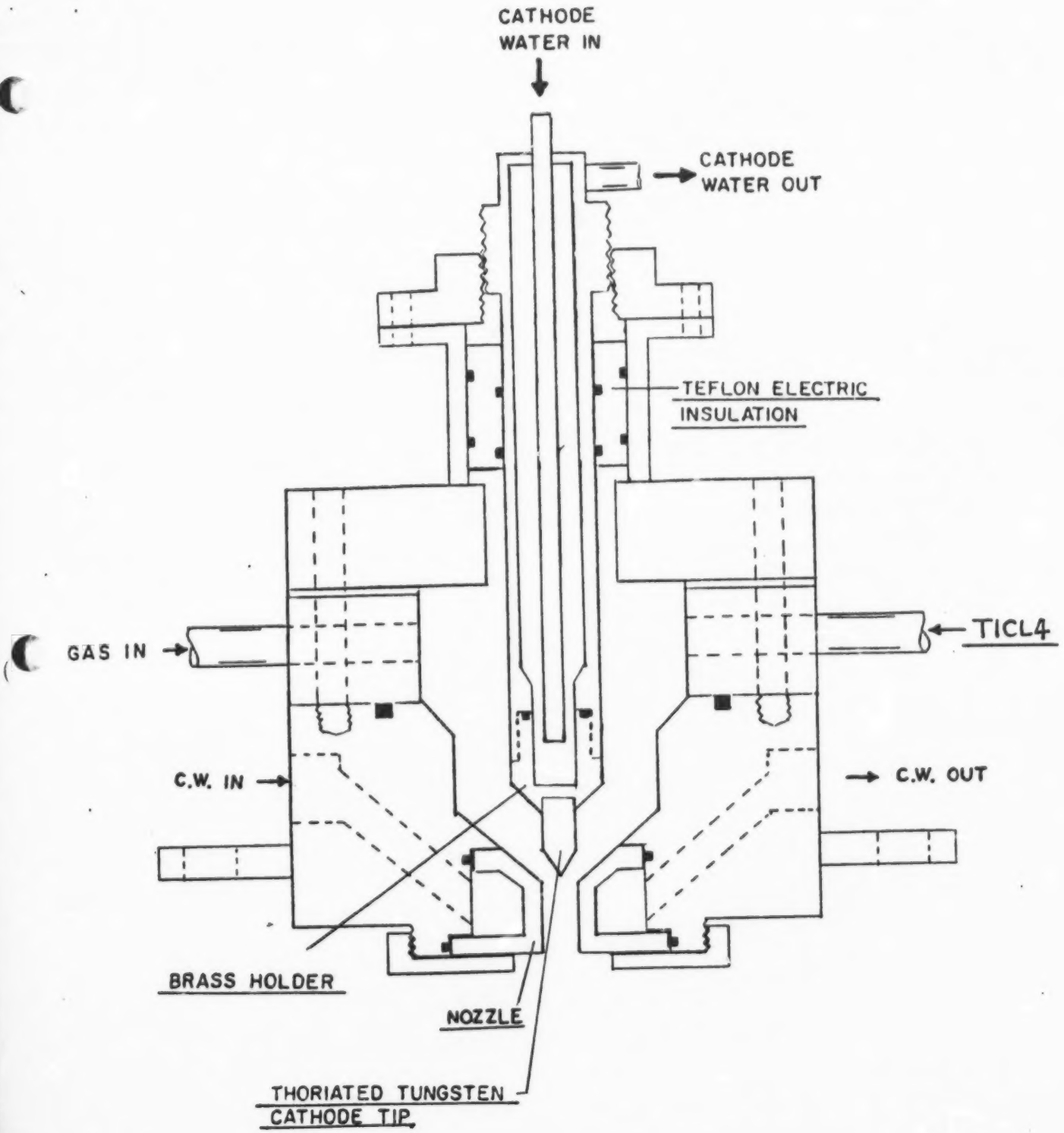
design. It comprised a water-cooled tungsten cathode recessed in an inner water-cooled concentric nozzle (made of copper) and-non-water-cooled gas feeding part (made of manel). The latter contained two tangential gas injection ports facing each other diagonally, one for $TiCl_4$ vapor and the other for argon. Two different nozzle orifice diameters of 6.3 and 7.1 mm respectively were used.

The cathode consisted of a brass tube acting as the cathode tip holder and a conical thoriated tungsten tip. An 'O'-ring was used to seal the joint of the two parts. Inside the brass tube, a stainless steel tube was silver-brazed at the top and extended to just above the top surface of the tungsten tip. Cooling water entering through the inner tube impinged toward the tungsten tip and then left the cathode via the annular space between the two tubes. A copper strip was attached to the top of the brass body, serving as a cathode electrical connection. A 2% thoriated tungsten rod (6.3 mm dia.) was silver-brazed to a brass holder and then the tip of the rod was grounded to a 60° angle.

The vertical position of the tungsten tip was adjustable via a fine threading and teflon sleeves with 'O'-rings were used for electrical insulation and to provide a gas-tight seal between the cathode and the nozzle.

FIGURE 8

CATHODE ASSEMBLY


CATHODE
WATER IN
CATHODE
WATER OUT
TEFLON ELECTRIC
INSULATION
GAS IN
TICL4
C.W. IN
C.W. OUT
BRASS HOLDER
NOZZLE
THORIATED TUNGSTEN
CATHODE TIP

RESULTS AND DISCUSSION

Preliminary Work

Considerable arc instability was a grave problem, which had to be tackled to obtain reliable operation. Initially, the mixture of argon and $TiCl_4$ vapor was used as a plasma gas to determine the degree of arc stability at various arc powers by using the cathode assembly shown in figure 2. As the feed rate of $TiCl_4$ vapor was increased at the constant rate of 10 L/min. of argon, the arc voltage began to fluctuate significantly. Various conditions of operation were tested, such as changing the arc power, the arc length and the $TiCl_4$ feed rate. No improvement in the arc stability were achieved.

A test was devised to check whether the used of a cold anode instead of the hot molten anode could stabilize the plasma because of the higher electrical conductivity of the former. No improvement in arc stability was observed.

A further test was performed to see if the presence of $TiCl_4$ vapor in the plasma causes the plasma stability by entrainment into the plasma column from a stream of the halide fed through a side port into the reactor. Again, no improvement in arc stability was observed.

Following several unsuccessful trials, the water-cooled nozzle was modified by welding a stainless steel-316 disc to the bottom of the nozzle. The disc had an opening (7 mm dia., 4 mm thick), and the cathode tip was recessed within the nozzle housing and positioned about 1 cm from the bottom of the disc. The rational for this arrangement was to provide what is called "wall stabilization". Three tests were conducted. In the first test, a cold anode and side feeding of the halide by entrainment were used. The plasma of a mixture of argon (18 g/min) and $TiCl_4$ (up to 7 g/min) was very stable within 1 volt of arc voltage fluctuation. No conversion to titanium was observed. In the second test, a hot molten titanium anode

replaced the cold anode in the first test. The plasma arc voltage was again stable for the same experimental conditions. Some metallization of the anode was noted, indicating the possible deposition of Ti along with some $TiCl_2$ (black) and $TiCl_3$ (blue). Very low conversion to titanium was estimated. The results from the above two experiments may be interpreted by the hypothesis that relatively small quantities of $TiCl_4$ vapor actually enter the plasma and are dissociated there. The poor Ti collection may also be due to metal vaporization from the hot zone and reverse chemical reaction between the liberated chlorine and the molten titanium in the latter.

In the last test, $TiCl_4$ was introduced tangentially into the cathode assembly and thus fed into the argon plasma. This is the preferred feeding method. The plasma was at first quite stable, but became unstable due to severe cathode tip erosion and damage to the nozzle opening.

On the basis of the information obtained so far, a water-cooled, wall-stabilized nozzle was designed and constructed (as shown in Figure 3). Difficulty was experienced with the new nozzle in arc initiation because of the longer arc gap in the set-up. A pilot arc circuit for easy arc initiation at longer arc gaps was completed and tested successfully. The arc was transferred to the anode instantaneously up to 4 cm of arc length. The value of the pilot arc resistor used for the test was 2.1 ohms at 1200 W rating and it was eventually increased to 2 ohms at 4200 W rating.

Two experiments were performed to check if stable plasma conditions could be established by adjustment of gas flow rats and arc power. In the first test, 10 L/min. of main plasma argon flow and about 1 g/min. of $TiCl_4$ were used. The arc voltage was about 48±2 volts, at 250 amperes, and an arc lengths of 3 to 5 cm. The test was successful and lasted for 45 minutes. In the second experiment, the same conditions as those in the first experiment were initially used, again with stable behavior of the plasma, indicating good reproducibility of the previous results. Once these stable conditions had been achieved, the $TiCl_4$ feed rate was increased. The arc voltage rose to 59 volts, at which point the arc extinguished itself.

Initially, it was thought that the arc extinction could be prevented if $TiCl_4$ flow rate had been gradually increased and adeguate power settings from the power supply had been made in time.

Experiments were performed to correct arc extinction at higher $TiCl_4$ feed rates. With small feed rates (less than 1 g/min.), the arc was stable up to around 55 volts (main argon flow rate: 15 L/min.; arc length: 4 cm; arc current: 350 A). When the $TiCl_4$ feed rate (2.5-5 g/min.) was increased, the arc current was increased rapidly to 500 A, so that a sudden arc voltage would not extinguish the arc. The latter eventually reached 66 volts at 450 A. The test was only terminated because of a short circuit, followed by a water leak from the nozzle and the sleeve surrounding the arc, as a result of double-arcing due to the high power used.

It was apparent at this time that the present set-up could not permit the determination of the exact operating conditions for successful stabilization of the arc at a reasonable rate of $TiCl_4$ feeding. It was therefore decided to postpone wall-stabilization studies until an appropriate research reactor had been designed and built. The necessary features to prevent arcing (by using a nozzle with a larger downstream diameter and more energetic cooling) will be incorporated in this new reactor.

In the meantime, the initial reactor chamber was modified to operate with a wide nozzle, no wall stabilization, and a mild vortex in the cathode assembly. The location of the exiting gas port was changed from its previous arrangement of four small lines in the bottom of the reactor, to larger diameter opening in the side of the reactor. Experiments were conducted with a shorter arc (3 cm or less) with controllable vacuum conditions (250-760 mm Hg). It was felt that these measures would provide a good degree of stability to the arc. The tests were unsuccessful because of the inability to sustain the arc for a reasonable period of time. It was considered to be quite possible that the deficiency of easily ionizable gas near the cathode tip, due to no wall constriction and air leakage to the chamber at lower pressure, could cause the arc instability.

Main Work

It was shown, in the preliminary work, that the establishment of pure $TiCl_4$ transferred-arc plasma with reasonable $TiCl_4$ flow rates was unsuccessful. The emphasis was, thus shifted from a transferred-arc to a non-transferred-arc.

Experiments were conducted to determine the conversion and yield of titanium at various operating conditions by using the experimental set up shown in Figure 9. The data obtained are summarized in Table I.

Experiments 3 through 8 were performed on the old reacting chamber, using argon as plasma gas and hydrogen as carrier gas. The best result from experiment 7 gave a conversion to titamium of 27%, assuming that the increase in the weight of the anode was solely due to the deposition of metal. A qualitative analysis by scanning electromicroscopy (SEM) showed traces of oxygen and nitrogen but no chlorine. Very fine needle-shaped crystals about 10-micron long were found around the boundary of the anode disc, where the heat transfer was lower. Diamond and/or doughnut-shaped crystals were obtained from the hotter central region of the anode disc. They were less than 10 micron in diameter (O.D.). The color of the crystal surface was a mixture of golden-yellow (probably TiN) and silver-grey, but below the surface, the color was all silver-grey, typical of titanium metal. In the runs 3 to 5, the significantly low conversion was considered to be caused by vapor leakage from the reactor head.

Nine experiments (9 to 17) were conducted to identify the optimum operating conditions to maximize the recovery of titanium under non-transferred arc mode. Results gave a maximum of 9%, with $TiCl_4$ feed rates varying between 0.5 and 3.8 g/min. It was observed that the metallic deposit on the partially molten anode disc consisted of needle-like crystals when an excess of H_2 was tangentially injected towards the titanium disc. The metal produced appeared to consist of diamond-like crystals. The product collected was too small for chemical analysis.

Figure 9

Schematic Experimental Plasma System

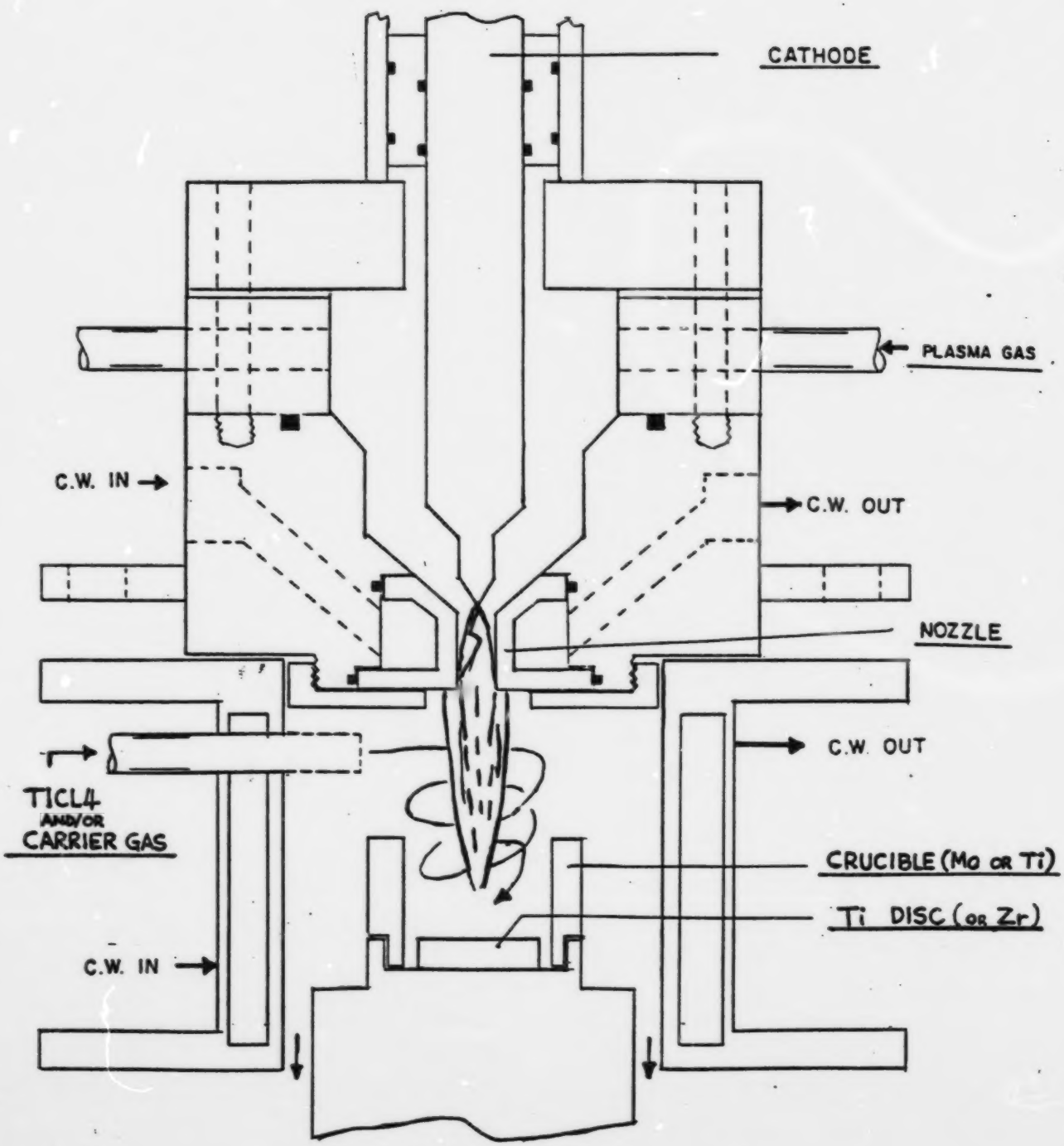

CATHODE
PLASMA GAS
C.W. IN
C.W. OUT
NOZZLE
C.W. OUT
TICL4
AND/OR
CARRIER GAS
CRUCIBLE (Mo OR Ti)
Ti DISC (OR Zr)
C.W. IN

TABLE I

Tabulation of Runs to Illustrate Conversion and Yield of Titanium in the plasma jet of a mixture of Argon, Hydrogen and Titanium Tetrachloride

Run N°.	1 I (A)	2 V (V)	3 P_o (KW)	4 Ar l/min)	5 H_2(Pri) (l/min)	6 H_2(Car) (l/min)	7 N_2(Pri) (l/min)	8 N_2(Car) (l/min)	9 $TiCl_4$ (g)	10 $TiCl_4$ (g/min)	11 t (min)	12 Ti (g)	13 Ti Conver-sion (%)	14 Boiler Temp (°C)
1	250	52±3	13	-	-	-	-	-	27.3	3.41	8	1	8	136
2	250	50±3	12.5	-	-	-	-	-	28.8	3.60	8	1.2	10	136
3	300	15	4.5	18.9	-	2.3	-	-	4.5	0.26	17	0.02	2	25
4	250	16	4.	18.9	-	2.3	-	-	28.6	4.1	7	0.03	1	139
5	300	14	4.2	18.9	-	2.3	-	-	19.3	1.3	15	-	-	-
6	275	14	3.85	14	-	1.4	-	-	4.6	0.26	18	0.06	5.2	50
7	300	16	4.8	18.9	-	2.8	-	-	17.8	0.99	18	1.23	27.3	139
8	300	16	4.8	18.9	-	2.0	-	-	4.0	0.24	17	0.1	10	25
9	300	16	4.8	14	-	3.5	-	-	10.2	0.44	23	0.22	8.6	93
10	300	15.5	4.7	14	-	3.5	-	-	16.0	1.6	11	0.13	3.3	120
11	300	15.5	4.7	14	-	3.5	-	-	37.8	3.78	10	0.15	1.6	93
12	300	15.3	4.6	14	-	3.5	-	-	9.5	0.95	10	0.12	5.1	93
13	350	15	5.25	14	-	3.5	-	-	18.8	0.94	20	0.07	1.5	93
14	300	15	4.5	14	-	3.5	-	-	9.6	0.64	15	0.1	4.2	93
15	300	15	4.5	14	-	3.0	-	-	10.3	2.1	5	0.1	3.9	93
16	300	15.3	4.6	10	-	2.0	-	-	33.0	4.13	8	-0.14	-	93
17	250	15.6	3.9	14	-	3.0	-	-	8.0	2.0	4	0.02	1.0	93
18	300	15	4.5	12	-	3.8	-	-	9.8	0.65	15	0.14	6.0	93
19	250	30	7.5	12	-	6.6	4.7	-	9.1	0.91	10	0.3	10.	93
20	250	25	6.25	12	9.2	2.4	-	-	88.5	8.85	10	0.85	4.	136
21	250	28.8	7.2	12	-	4.0	0.71	-	5.0	0.33	15	0.64	39.6	93
22	225	34	7.65	12	9.3	3.0	-	-	23.0	2.3	10	1.24	21	93
23	250	21	5.25	12	6.6	2.4	-	-	1.0	0.1	10	0.18	72	93
24	250	24	6	12	6.6	3.0	-	-	8.0	0.8	10	0.28	14	93

It was suspected that the cause of the poor metal conversion was due to the excessive boiling of the titanium disc and consequent loss of metal produced. Two different crucibles (made of molybdenum and of titanium, respectively) were tried. It was found that there was a significant deposit on the walls of the titanium crucible but the conversion was not increased accordingly. As a matter of fact, the two tests (runs 16 and 17) showed the removal of titanium from the original titanium button. The reasons may be due to simple metal vaporization from the hot zone or a back reaction between titanium and $TiCl_4$ to form $TiCl_2$.

In experiment 13, a lower conversion was observed when a zirconium button replaced the titanium button in the crucible, implying a preferential selectivity of the dissociated titanium to the molten titanium.

Seven experiments (18 to 24) were performed to improve titanium metal conversion. It was found that the metal conversion increased significantly from 4.6 to 72% as the $TiCl_4$ feed rate was decreased from 9 g/min. to 0.1 g/min. This might confirm the difficulty of obtaining good metal conversion at reasonable feed rates. However, analysis of the product by X-ray diffraction showed the presence of TiN, probably resulting from exposure to air.

As a result of the above observation, four tests were performed to produce TiN in the non-transferred arc mode with $Ar-N_2$ plasma. In the first test, the $TiCl_4$ vapor was entrained by H_2 and the powder product consisted mainly of needle-shaped crystals, golden yellow in color. In the second test, nitrogen was used as the carrier gas, and no TiN was produced. In a third test, an $Ar-H_2$ plasma was used, with nitrogen as the carrier far $TiCl_4$. In the last test, an $Ar-H_2$ plasma was used with argon as the carrier gas. In the last two tests, golden yellow powder was produced. The conversion to TiN ranged from 14 to 40%. X-ray diffraction showed the presence of TiN as a major product, along with weak peaks of TiO, TiO_2 and titanium. It was suggested that a reductant (like H_2) must be present to permit the formation of the nitrides.

CONCLUSIONS

The following conclusions can be made through the work performed during phase II of the project:

1. Pure $TiCl_4$ transferred-arc plasma can be successfully generated at lower $TiCl_4$ flow rates (~2 g/min.) and a plasma process of producing titanium metal from the plasma dissociation is technically demonstrated on a molten anode surface.

2. The economic feasibility of such a process is not established because of inability to generate a stable plasma at much higher $TiCl_4$ flow rate (~50 g/min.).

3. It was not possible to establish stable operating conditions for pure $TiCl_4$ or a mixture of argon and $TiCl_4$ transferred-arc plasma with reasonable flow rates (~10 g/min.). It appears that a critical $TiCl_4$ flow rate exists a given arc condition from the point of view of arc stability. It also appears that the energy required for the dissociation of larger amounts of $TiCl_4$ cannot be provided with the existing rectifier.

4. Titanium can be produced from a mixture of $TiCl_4$ and H_2 introduced into a non-transferred argon plasma. The metal conversion increased significantly from 4.6 to 72% as the $TiCl_4$ feed rate was decreased from 9 to 0.1 g/min. However, the production rate was too low and its commercial feasibility was not established.

5. It appears that the plasma process can be applied to the production of TiN.

6. A detailed study of the plasma physics should be made to provide additional information leading to possible establishment of stable and pure $TiCl_4$ plasmas at realistic halide flow rates.

7. From an operational point of view, the design and constructional details of the plasma systems such as the cathode assembly and the feeder of the halide vapor were found to be very effective. However, the development of a reliable product collecting system should be undertaken so that higher metal conversion, with non contamination by impurities, can be attained.

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